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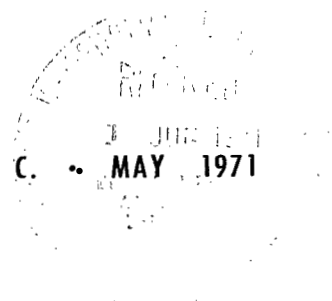


SHORTING PATH MODE OF DEGRADATION
IN COPPER SULFIDE - CADMIUM
SULFIDE THIN-FILM SOLAR CELLS

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16. Abstract Copper sulfide - cadmium sulfide thin-film solar cells were subjected to dark forward bias tests and tests under air-mass-one illumination while in the open-circuit condition. The solar cells were observed to degrade from 20 to 50 percent in maximum power, from 5 to 10 percent in open-circuit voltage, and from 50 to 95 percent in shunt resistance. Associated with the degradation due to these tests was the appearance of hotspots on the cells and metallic copper on the surface of and within the cells. The degradation mechanism for these two test conditions was determined to be the formation of copper filaments between the grid contact and substrate, which resulted in shorting paths within the cell.					
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SHORTING PATH MODE OF DEGRADATION IN COPPER SULFIDE - CADMIUM SULFIDE THIN-FILM SOLAR CELLS

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SUMMARY

Changes in the electrical characteristics and cell surface temperatures of copper sulfide - cadmium sulfide thin-film solar cells were studied. The solar cells were observed to degrade in air at 298 K under illumination by leaving the cells in the open-circuit condition and in the dark by applying a forward bias. Changes in cell surface temperature were monitored during and after degradation by means of an infrared viewing device and by temperature-sensitive liquid crystals. Suspect regions of the cells were cross-sectioned and examined by photomicrography.

The experiments have shown that cells exposed to air-mass-one illumination (100 mW/cm^2) for several hundred hours while open-circuited degrade principally by a decrease in shunt resistance. The shunt resistances of some cells tested were reduced by 50 to 95 percent after 260 hr of illumination. Reductions of 20 to 50 percent maximum power and 5 to 10 percent in open-circuit voltage were also observed. The short-circuit current was least affected by the test and showed reductions of less than 5 percent.

Accelerated cell degradation was produced by subjecting the cells to dark forward biases with a current flow of 0.5 to 1.0 A for several minutes. Cells degraded in this manner showed, under illumination, reductions in shunt resistance, maximum power, and open-circuit voltage similar to cells degraded by constant illumination. No change in short-circuit current was observed.

Associated with the degradation due to these tests was the appearance of hotspots on the cells and of metallic copper on the surface and within the cell. The degradation mechanism for these two test conditions was determined to be the formation of copper filaments between the grid contact and the substrate resulting in internal shorting paths. These internal shorts caused a reduction in the shunt resistance and consequently a degradation in dark diode and photovoltaic performance. The high current densities flowing in these localized shorts appeared as hotspots on the cells.

INTRODUCTION

Copper sulfide-cadmium sulfide (Cu_2S - CdS) thin-film solar cells have been tested in simulated space environment conditions since 1964 (ref. 1). The results of these tests show that in general the solar cells are degraded by long-term temperature and light cycling. The exact nature of the degradation mechanism had not been determined partly because of the length of the tests and the inaccessibility of the cells during the tests. In order to identify the degradation mechanism, cells were tested under special conditions. These tests were to identify weaknesses in the cells and ultimately to determine whether they are related to the degradation observed in the simulated space tests. For example, it had been found that cells degraded more rapidly and more severely when illuminated while at open-circuit voltage than when loaded at the more normal condition of maximum power (ref. 2). Also, cells under external bias had been observed to develop hotspots which could be detected with an infrared viewing device (ref. 3).

It was of interest to determine if the appearance of hotspots which occurs when an external bias is applied without illumination is related to the degradation of electrical power from the solar cells, which occurs under open-circuit illumination. Therefore, an experimental study was conducted to examine simultaneously the temperature patterns on the solar-cell surface and the electrical performance under special testing conditions. Since Cu_2S - CdS solar cells are degraded most rapidly at high load voltages, the illumination tests were conducted with the cells open-circuited. Also, in order to observe temperature patterns with the infrared detector during the course of the tests, the tests were conducted in air instead of vacuum. The cells were held at 298 ± 1 K to avoid changes in the cell which occur when they are heated in the presence of oxygen. This report describes the observations made on cells tested under constant illumination at open-circuit voltage and under external bias voltages in the dark.

The report also deals with the formation of copper nodules. In the course of reproducing the degradation effects, investigators at the Clevite Corporation discovered that copper nodules plate out on the Cu_2S surface of cells subjected to illumination while open-circuited (ref. 4). Tests then were conducted at the Lewis Research Center to determine the source of the copper nodules and their relation to the hotspots and degradation of the solar cells under illumination and external bias tests.

SYMBOLS

AM1 air mass one, spectral distribution and intensity of sunlight on Earth at sea level with Sun directly overhead and passing through a standard atmosphere

AM0	air mass zero, spectral distribution and intensity of sunlight in near-Earth space without atmospheric attenuation
I	current, A
I_{SC}	short-circuit current, A
P_M	maximum power, W
R_{SH}	shunt resistance, ohms
V	voltage, V
V_{OC}	open-circuit voltage, V

APPARATUS

Solar-Cell Test Apparatus

This apparatus consists of a water-filtered tungsten light source, a temperature-controlled block with vacuum openings to hold cells in place, and an electronic load which varies the load across the cell from V_{OC} to I_{SC} . An X-Y plotter was used to record the I-V curve. The intensity of the tungsten light source is adjusted to a solar intensity of 136 mW/cm^2 with an airplane flown CdS standard cell (ref. 5) prior to I-V measurements. Standard cells are select 1- by 2-cm CdS cells which are operated only in the I_{SC} condition when used and are stored under dark and zero humidity conditions when not used. The conditions of cell area, operation, and storage greatly minimize the degradation problems observed for cells operated under "actual use" conditions. To date no standard cell has shown changes in I_{SC} .

The light intensity is reproducible to ± 0.3 percent of one solar constant and the estimated light uniformity over the test plane is ± 2 percent. Based upon an analysis-of-variance study (ref. 2), the standard deviations of the V_{OC} , I_{SC} , and P_M are $\pm 1.3 \text{ mV}$, $\pm 2.1 \text{ mA}$, and $\pm 2.8 \text{ mW}$, respectively.

Transistor Curve Tracer

This instrument was used to bias the cells. The applied voltage across the cell is swept from zero to a preselected peak voltage at a frequency of 120 Hz. The instrument contains a cathode ray tube which displays the I-V characteristic while the cell is under bias.

Infrared Viewing Device

The infrared device used to view temperature changes on the cell surface is shown in figure 1. The field of view of the camera is 5° by 5° , and the display unit frame size is 42 by 54 mm. Spatial resolution of the display is 0.5 mm, and the thermal resolution is about 0.2° C (ref. 6). A photograph of the display, called a thermogram, is obtained by using a photographic camera for a permanent record of the image.

Temperature-Sensitive Liquid Crystals

Changes in the temperature distribution of cell surfaces were also detected with cholesteric liquid crystals sensitive in the 40° to 42° C temperature range. The commercially produced crystals were applied in the form of a thin film with an airbrush. A description of the properties and uses of the liquid crystals is given in reference 7.

DEGRADATION DUE TO UNILLUMINATED EXTERNAL BIAS AND CONSTANT-ILLUMINATION OPEN-CIRCUIT LOAD TESTS

Experimental Procedure

Unilluminated bias tests. - Unilluminated forward and reverse bias tests of the Cu_2S -CdS solar cells were made on approximately twelve cells manufactured in April and May of 1968. A complete description of the type of CdS solar cell used in this study is given in reference 8. The I-V characteristics were displayed for several seconds on the curve tracer and were photographed for record. During biasing, the temperature patterns of the cells were monitored with the infrared viewing device as well as with liquid crystals. Depending on the thickness of the liquid crystal coating and the bias level, hotspots as small as $50\text{ }\mu\text{m}$ in diameter were observable with a microscope.

Constant-illumination tests. - Constant-illumination, open-circuit load tests were made on four cells randomly selected from cells produced in September 1968. Three of the four cells had not been tested previously except for the measurement of the I-V characteristic at the time of fabrication. Since fabrication, the cells had been kept in dry, dark storage. In a preliminary experiment the fourth cell was tested under constant illumination while open circuited, for about 6 days. It degraded during the test and recovered during dark storage.

Prior to the constant-illumination tests reported here, the following measurements were made on the four cells. The dark I-V characteristic was measured between 200 and -25 mA. The temperature distribution of the cells was checked with the temperature viewing device during the dark measurement and while the cells were illuminated with simulated sunlight of AM0 intensity. The illuminated temperature distribution check was made with the cells held momentarily at I_{SC} and V_{OC} . Finally, the illuminated I-V traces were made. The cells then were exposed to constant illumination of approximately AM1 intensity for 260 hr. During illumination, the cells were in air at ambient pressure and humidity and were held at 298 ± 1 K. The cells were open-circuited except during the periodic electrical measurements when the load was varied momentarily from V_{OC} to I_{SC} to record the I-V characteristic. The light intensity was raised to the AM0 value whenever an I-V characteristic was measured. Values for I_{SC} , V_{OC} , and P_M were obtained directly from the I-V traces. Values for the R_{SH} were approximated from the slope of the I-V trace at I_{SC} . Thermograms of each cell were also made periodically.

After the constant-illumination period, the light source was shut off and the cells were covered with black paper. Otherwise, cell conditions were the same as during the light period. The cells were kept in the dark for 163 hr with only occasional interruptions for checking the I-V characteristic which required illuminating the cells for a few minutes. The cells were then subjected to an additional 334 hr of constant illumination during which the procedures and conditions were the same as the initial light period. At the completion of the second light period, illuminated and dark I-V measurements were made for comparison with the pretest measurements. The cells were then sprayed with liquid crystals to define more clearly the temperature distribution on the cell surface.

Results and Discussion

Unilluminated bias tests. - The dark I-V characteristics of Cu_2S -CdS solar cells changed when a forward current of 0.5 to 1.0 A was applied to unilluminated cells. The voltage across the cells was 1.0 to 1.75 V.

Figure 2 shows the initial and degraded dark I-V curves of a typical cell. Within minutes after the bias was applied, the I-V characteristic began a gradual transition toward the ohmic state. Primarily, the dark shunt resistance decreased, so that at a fixed voltage, the current increased. This manner of change suggests that a bias-induced shorting path was forming which was shunting the barrier layer. During this period, at least one circular or elliptical hotspot appeared on the cell surface. The hotspots, which were not present initially, always coincided with a cell grid wire and were usually located near the edges of the cell. This gradual transition was followed by an interme-

diate stage in the degradation process in which the I-V curve fluctuated randomly between an ohmic and a rectifying characteristic. Finally, the cell formed a stable ohmic curve and a single hotspot. The total time for this cell to degrade was less than 15 sec, but this varied from cell to cell with some cells taking several minutes before degradation began. Thermograms taken before and after degradation show the resulting hotspot (fig. 3). Increasing the forward bias to 3 A did not affect the ohmic I-V curve. The increase, however, did increase the temperature and diameter of the hotspot. Hotspot temperatures in excess of 398 K were detected for some cells passing a current of about 1 A.

When a reverse bias of about -1.0 A, at -0.5 V, was applied to the degraded cell, an abrupt recovery of rectification occurred within a few seconds (fig. 2). The I-V curve was improved, in comparison to the initial trace, in both the forward and reverse directions. The rapid recovery, similar to a switching phenomenon, was accompanied by the disappearance of the hotspot. Just prior to recovery, the hotspot momentarily increased in temperature and then disappeared. Usually, a small translucent bubble appeared under the cell cover plastic where the hotspot had been located. The degradation-recovery process was repeatable and was always accompanied by the formation of a hotspot at a new location, usually in the vicinity of the previous one.

The photovoltaic I-V characteristic is shown in figure 4 for a typical cell before and after unilluminated forward bias degradation. The characteristic after reverse bias recovery is also shown. The cell in the degraded state clearly shows the effects of a low shunt resistance. There is a loss in maximum power and open-circuit voltage. The thermogram (fig. 5) of the open-circuited cell exposed to about 70 mW/cm^2 illumination shows the hotspot in the same location as it appeared under unilluminated forward bias. Increasing the intensity of illumination also caused an increase in hotspot temperature and diameter. These effects suggest that unilluminated forward bias degradation is a result of shorting path formation.

As shown in figure 4, successive retraces (short dashed lines) of a degraded cell induce a slight recovery in the photovoltaic characteristic. These retraces, however, produced little or no improvement in the dark I-V curve. This suggests that the photovoltaic I-V trace may be a more sensitive indicator of recovery processes. The hotspot appeared unaffected by the slight recovery.

The dark and photovoltaic characteristics could be fully restored by cutting out the hotspot area. The long and short dashed curve in figure 4 shows the restoration of the photovoltaic I-V characteristic by this method. The loss in I_{SC} is accounted for by the loss in cell area due to excision of the hotspot. The same cell was degraded several more times, and the process was always accompanied by the formation of hotspots. Excision of the hotspot always recovered the cell, as evidenced by its dark and photo-

voltaic characteristics. In general, the ability to restore a degraded cell by excision of the hotspot indicates that the degradation process occurs only in a local cell region.

Constant-illumination tests. - The effect of constant-illumination open-circuit conditions on the photovoltaic I-V curve of Cu_2S -CdS solar cells is shown in figure 6. The curves show the initial cell output and the output after 4, 9, and 11 days. This type of change in the I-V curve is generally attributed to a decrease in the shunt resistance of the cell. Decreases in R_{SH} of 50 to 95 percent were noted for the four cells tested. Reductions in P_{M} of 20 to 50 percent and in V_{OC} of 5 to 10 percent also occurred. Accompanying this degradation was the appearance of hotspots. The hotspots disappeared during the measurement of the I-V curve. This disappearance occurred between the maximum power and short-circuit current. When the cells were returned to V_{OC} , the hotspots reappeared.

These changes (i.e., the decrease in R_{SH} and the appearance of hotspots as a result of the open-circuit illuminated test) are similar to the changes observed in the unilluminated forward bias tests. The loss of shunt resistance in both cases strongly suggests the formation of localized shorting paths across the barrier. When the shorting paths are present and the cell is near open circuit, much of the current from the cell passes through the shorts and produces hotspots. As the voltage is decreased in measuring the I-V characteristic, the power dissipated in the shorts is rapidly reduced and the hotspots disappear.

The effect of dark storage on a cell degraded by the illuminated open-circuit test is shown in figure 7. The curves show the initial output prior to degradation, the cell output at the end of the constant-illumination test, and the output after 3 and 6 days of dark storage. As mentioned in the description of the unilluminated forward bias tests, measuring the I-V characteristic produces in itself some recovery in the degraded cells. Therefore, part of the recovery during the dark storage can be attributed to the I-V measurement used to monitor the cell. Thus, the wiggle in curve c is attributed to abrupt recovery while the I-V curve was being traced.

The I_{SC} , V_{OC} , and P_{M} of three of the four cells tested were restored to within 95 percent of the initial values. The remaining cell, which was the cell that had been tested in an earlier experiment, only recovered to 82 percent of the initial P_{M} . The cells also showed some recovery in R_{SH} due to dark storage. The cell represented in figures 6 and 7 had an initial R_{SH} of 17 ohms, which decreased to 1 ohm during the test. After dark storage, the R_{SH} was 12 ohms. This indicates that the shorting paths which resulted from the illuminated test were only partially removed because of the dark storage. However, the increase in R_{SH} from 1 to 12 ohms was sufficient to make the hotspots disappear.

Since the R_{SH} was not recovered entirely by dark storage, one might expect the cell to decrease in output at a faster rate when subjected to a second illuminated open-

circuit test. Figure 8 shows the changes in the electrical performance as a function of time for one of the cells tested. During the first illuminated period, it took 180 hr for the P_M to decrease by 25 percent. After recovering in the dark to 95 percent of the initial value, the cell was again placed on test. This time the P_M decreased by 25 percent in only 68 hr. Although the rate at which the cells degraded varied from cell to cell, all the cells degraded in less time during the second illuminated open-circuit test than during the first. The hotspots which appeared during the first test also reappeared in the same location during the second test. Dark storage of cells degraded under illuminated open-circuit tests, therefore, provides only temporary recovery of the electrical performance. Indications are that the cell will degrade faster in subsequent testing periods.

In addition to the degradation of the photovoltaic I-V characteristic discussed previously, changes in the dark I-V characteristic were also observed. Shown in figure 9 are the I-V plots of one of the cells tested. Originally all of the cells had a "normal" dark I-V trace such as the solid curve. After the constant-illumination tests, two of the four cells tested had ohmic dark I-V traces, such as the dashed curve. A third cell had become less rectifying. The remaining cell was not measured, since it was damaged during removal from the test fixture.

HOTSPOTS AND COPPER NODULES

Experimental Procedure

Constant-illumination tests. - With the discovery at the Clevite Corporation of copper nodules on Cu_2S -CdS solar cells tested at constant illumination while open-circuited (ref. 4), a microscopic examination was made of the four cells degraded by the constant-illumination test discussed previously. Special attention was given to the regions of the cells which had produced hotspots. When no evidence of copper could be found on the cell surfaces, additional cells were placed on test. In these tests five cells, Clevite and Lewis Research Center type, were loaded at open circuit while under constant illumination for about 100 hr. A tungsten lamp filtered through infrared reflecting glass and adjusted to an intensity of approximately AM0 was used as the light source. The cells were mounted on a water-cooled aluminum block. The cell temperature was monitored by a thermocouple mounted on the cover plastic and ranged from 30⁰ to 50⁰ C. The photovoltaic I-V characteristics of cells were taken before and after exposure to monitor the photovoltaic degradation.

Unilluminated bias tests with point contacts. - Attempts to grow metallic deposits also were made by biasing unilluminated cells which had no grids and no cover plastics.

Solid-gold-point-contact electrodes were used to make electrical contact with the cell surface and with the substrate tab. Constant forward and reverse bias voltages were applied to the cells through these point electrodes and the current was monitored.

Hotspot cross sectioning and analysis. - Using the techniques described in reference 9, various samples of cells subjected to tests described previously were cross-sectioned. Some samples were prepared with electrical leads accessible for biasing. The temperature pattern of these latter samples was determined by applying liquid crystals to the polished cross-sectioned surface while the cells were forward biased. Photomicrographs were taken, and the temperature distribution was monitored with liquid crystals after removal of each 10- μ m (0.4-mil) increment from the cross section.

In order to identify the metallic deposits on and in CdS solar cells which were subjected to tests discussed previously, three analytical tools were used. The first was an electron microprobe analysis. This technique identifies elemental substances in polished samples by detection of characteristic X-rays resulting from high-energy electron excitation. The second tool was X-ray diffraction. In this method, the composition of samples is determined by analysis of scattered X-ray intensities. The third method, which is the least exact, is preferential etching. Polished samples were etched with different etchants and microscopically examined. The etchant used to identify CdS was a 15-percent solution of hydrochloric acid, and the etchant used to identify copper was a solution of five parts ammonium hydroxide, five parts water, and two parts hydrogen peroxide. Aqua regia was used as an etchant for gold.

Results and Discussion

Constant-illumination tests. - Within 100 hr after the cells were placed on test, the photovoltaic characteristics were degraded. The type and degree of degradation was as described previously and shown in figure 6. Hotspots and metallic deposits in nodule form appeared on the surface of the cell. The top view of a typical nodule is shown in figure 10.

A cross-sectional photomicrograph of a piece of a Clevite cell containing a nodule is shown in figure 11. The nodule, resting on the surface of the copper sulfide adjacent to the gold-plated copper grid, has pushed up the cover plastic. An electron microprobe analysis identified the nodule as elemental copper. Subsequently, a nodule was removed from the surface of the cell, and X-ray diffraction analyses confirmed that the nodule was copper. Preferential etching with a copper etch also showed many other nodules to be copper.

The number of nodules formed and their location varied from cell to cell. Usually, at least 1 nodule, and occasionally clusters of up to 40 nodules, appeared. The clusters of nodules were typically grouped over an area of about 20 cm^2 , usually near the periphery of a cell.

As shown in figure 12, all cells developed hotspots, which were detected by liquid crystals. The hotspots always coincided with grid wires, whereas the copper nodules were observed between the grid wires.

No difference in nodule growth or hotspot formation was observed that could be ascribed to differences in substrate or grid material. Comparable results were obtained on cells with molybdenum or zinc-silver substrates or with solid-gold and gold-plated copper grids. Copper nodules were grown on cells which had no copper other than that in the copper sulfide. Therefore, the elemental copper must be the result of decomposition of the Cu_2S .

As reported previously, however, no evidence of copper was seen on the surface of the four cells degraded by constant-illumination, open-circuit load. The hotspots which appeared on these cells were postulated to be due to shorting paths. Since the physical nature of these paths might now be explained as due to the deposition of copper filaments within the semiconductor material, a possibility that had certainly been established with the observation of surface nodules, it now remained essential to determine if copper filaments existed within the degraded cells. Consequently, one of the four cells was cross sectioned in the regions that developed hotspots. Careful examination of the cell in this manner revealed not only small copper nodules (fig. 13) that went undetected during microscopic surface examination, but also large copper inclusions in the shattered CdS under the grid (fig. 14). In two other instances, copper nodules, which were in contact with a grid wire, were found at a hotspot site under microscopic examination.

Hotspot cross sectioning and analysis. - A portion of a cell, about 6.5 cm^2 , containing an active hotspot and a hotspot that had been deactivated by reverse biasing was cross-sectioned. The active hotspot, similar to the one shown in figure 12, was also observed with liquid crystals on the polished cross-sectioned surface while the cell was forward biased. However, continued polishing caused this hotspot to disappear. A photomicrograph of a subsequent cross section of that area of the cell is shown in figure 15. A bundle of copper filaments can be seen extending from the gold epoxy to the substrate. The lamellar crack in the CdS portion of the cell shown in figure 15 was caused and propagated by the constant flexing of the cell during handling of the cell sample while a large number of polishes were made. It is believed that the propagation of the lamellar crack severed the filament, as shown in figure 15, and lead to the abrupt disappearance of the hotspot.

Lapping and polishing of cross sections was done in the region of the deactivated hotspot also. A cross-sectional photomicrograph of this region is presented in figure 16.

Comparing this region with the region of an active hotspot shown in figure 15 reveals sharp differences. In figure 16, the deactivated hot region is characterized by a large cavity in the CdS extending to the substrate. In addition, the fine-grained CdS near the crater bottom contained silvery and copper-colored metallic inclusions. Simple etching procedures did not unambiguously identify these particles. Other techniques which would normally be used to identify such particles could not be tried since they required that the sample be demounted and the experiment concluded.

The presence of such a localized disordered region can be the result of a very high temperature process. A likely process would be the fusing of a copper filament, like the one shown in figure 15, under strong reverse bias. The destruction of this filament, if it were a shorting path, would account for the observed disappearance of the hotspot.

Unilluminated bias tests with point contacts. - Dendritic copper deposits were formed on uncovered and ungridded Clevite and Lewis Research Center cells while in the dark. The copper appeared under the reverse biased (negative) probe in contact with the copper sulfide. Initial current levels for various applied voltages were in the milli-ampere range, but increased significantly during the bias periods.

Dendritic copper deposits appeared on the copper sulfide under the point contact for the reverse bias values of 2.5 and 0.38 V. No copper was seen at a 0.35-V reverse bias. Figure 17 shows a copper dendrite which appeared for the 2.5-V case. The elliptical area appearing slightly darker compared to the surrounding copper sulfide was typical of dendrite formation areas. Cross sectioning through a dendrite showed the copper only on the surface. Penetration of the dendrite into the CdS film was not observed.

During a 70-hr unilluminated forward bias test, the current passing through the uncovered cell increased substantially. At the conclusion of the test a discoloration was noticed on the copper sulfide surface. It was similar to the discoloration noted in the copper dendrite growth process but much smaller. Cross sectioning of the cell region directly under the point contact revealed no metallic deposits.

SUMMARY OF RESULTS

A study of the shorting path mode of degradation in copper sulfide - cadmium sulfide (Cu_2S -CdS) thin-film solar cells produced the following results:

1. Exposure of Cu_2S -CdS solar cells, usually for less than a minute, to a forward bias of 0.5 to 1.0 A while unilluminated resulted in the following changes:

- a. The dark I-V characteristic became ohmic, and subsequent measurements of the photovoltaic properties showed reductions in shunt resistance, maximum power, and open-circuit voltage. No changes in short-circuit current occurred.

b. Hotspots appeared on the cells. When these hotspots were examined by cross-sectional photomicrographs, copper inclusions were found within the semiconductor material. In one case, filaments of copper were found which extended from the gold epoxy grid contact to the substrate.

c. Cells degraded by the unilluminated forward bias conditions were recovered by reverse biasing the cells with 1.0 A, at 0.5 V, for a few minutes or by cutting out the deteriorated region indicated by the hotspot.

2. Exposure of Cu_2S -CdS solar cells for hundreds of hours to air-mass-one, simulated sunlight while open-circuited resulted in the following changes:

a. The dark I-V characteristic became less rectifying and in some cases became ohmic. The photovoltaic properties showed reductions of 50 to 95 percent in shunt resistance, 20 to 50 percent in maximum power, 5 to 10 percent in open-circuit voltage, and less than 5 percent in short-circuit current.

b. Hotspots and nodules of copper formed on the surface of the cells. Most of these nodules did not act as hotspots. Hotspots resulted from copper nodules touching or growing under a grid wire. Cross-sectional photomicrographs of the hotspots revealed copper inclusions and filaments within the semiconductor. Hotspot and nodule formation were independent of the grid and substrate material.

c. Losses in maximum power and open-circuit voltage from cells degraded by open-circuit constant-illumination tests were recovered to within 95 percent of the pretest values in most cases by storing the cells in the dark. The shunt resistance recovered to 58 percent of its initial value. As the cell output recovered, the hotspots disappeared.

3. Reverse biasing the Cu_2S -CdS region with point contacts resulted in copper dendrite growths on the Cu_2S surface for voltages of 2.5 and 0.38 V. Copper dendrites did not form at a reverse bias of 0.35 V. A forward bias across the Cu_2S -CdS region did not cause copper dendrite formation.

CONCLUSIONS

Subjecting Cu_2S -CdS solar cells to a dark forward bias or to illumination while open-circuited produces a loss in output characteristic of a reduced shunt resistance. In both cases, elemental copper is deposited on or within the semiconductor material. The source of this copper is the decomposition of Cu_2S . The potential for this reaction is provided by the photovoltage in the illuminated test and the external bias in the dark

test. Filaments of copper extending from the grid contact to the substrate provide the low-resistance shunt paths which reduce the photovoltaic output and appear as hotspots on the solar cell.

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Cleveland, Ohio, February 25, 1971,
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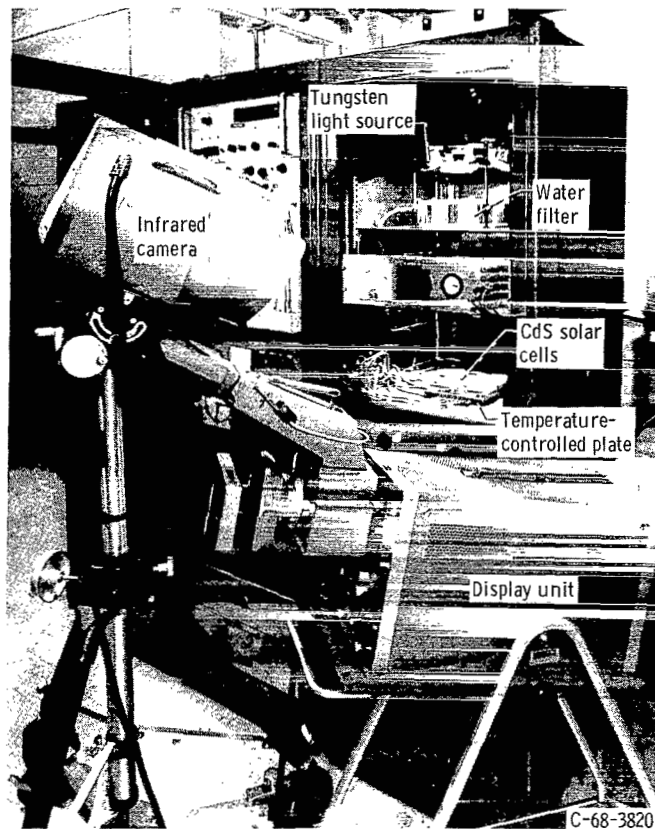


Figure 1. - Solar-cell test apparatus and infrared viewing device.

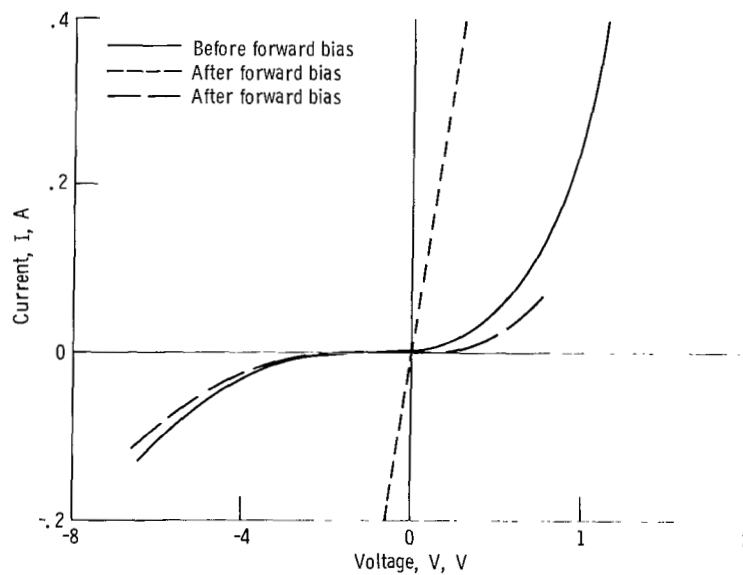
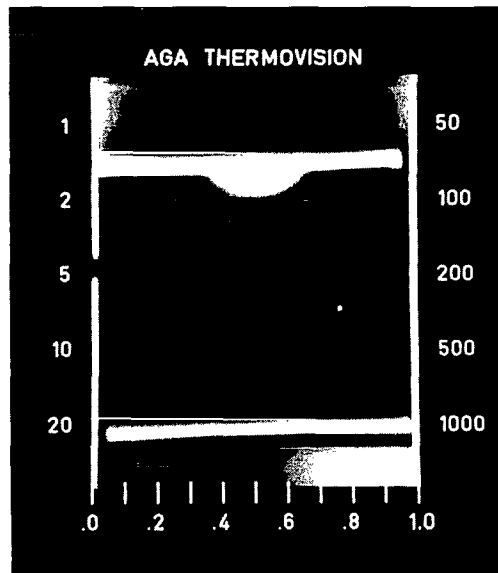
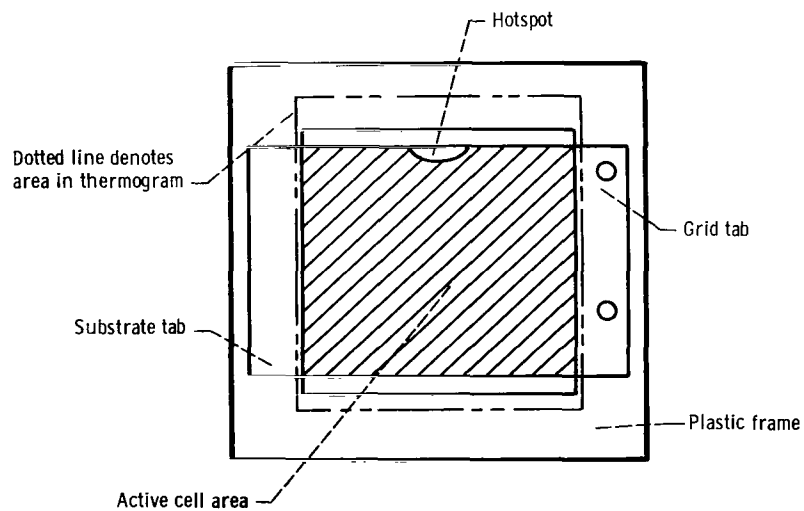


Figure 2. - Dark current-voltage characteristics of Cu_2S -CdS solar cell.



(a) Thermogram.



(b) Schematic showing area in thermogram.

Figure 3. - Hotspot appearing on cell degraded by forward bias.

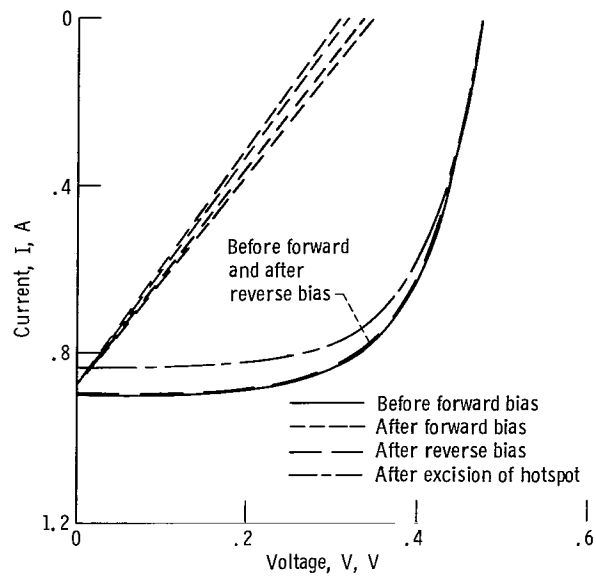


Figure 4. - Photovoltaic current-voltage characteristic of $\text{Cu}_2\text{S-CdS}$ solar cell.

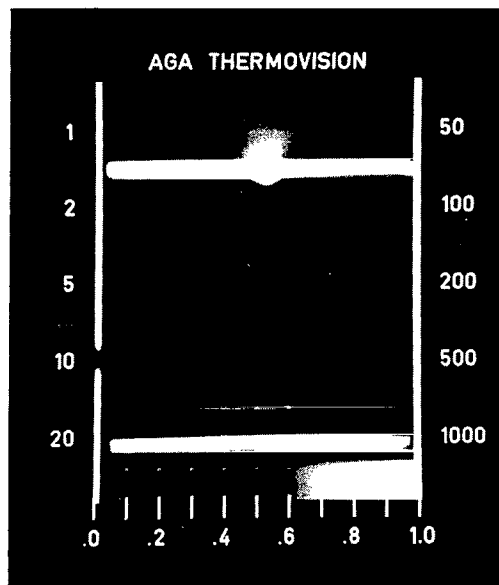


Figure 5. - Hotspot appearing on cell illuminated at 70 mW/cm^2 .

	Open-circuit voltage, V_{OC} , V	Short-circuit current, I_{SC} , A	Maximum power, P_M , W	Shunt resistance, R_{SH} , ohms	Voltage, V
————	0.477	0.816	0.266	17	Initial I-V trace
- - - -	.467	.810	.220	4	After 4 days on test
————	.454	.787	.173	2	After 9 days on test
- - - -	.435	.789	.131	1	After 11 days on test

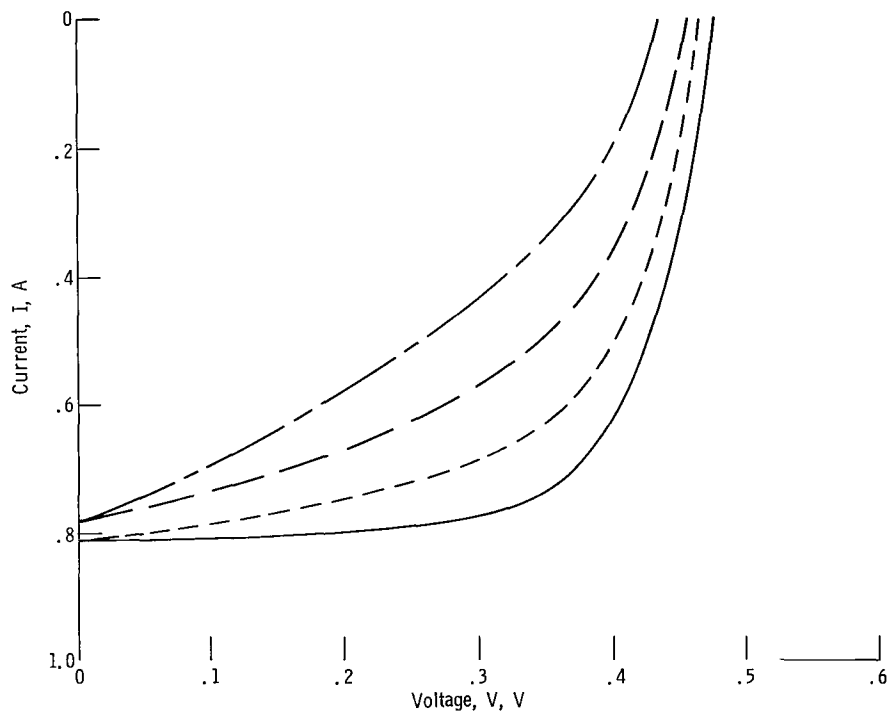


Figure 6. - Degradation of current-voltage characteristic during constant-illumination tests.

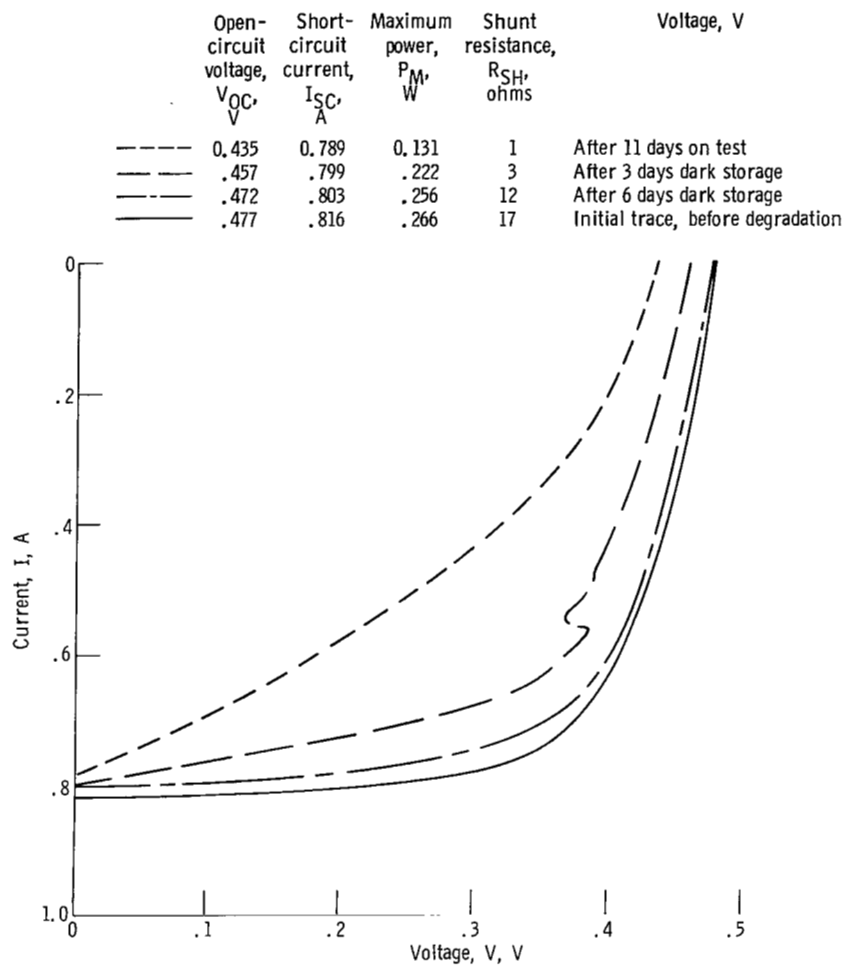


Figure 7. - Recovery of current-voltage characteristic during dark storage.

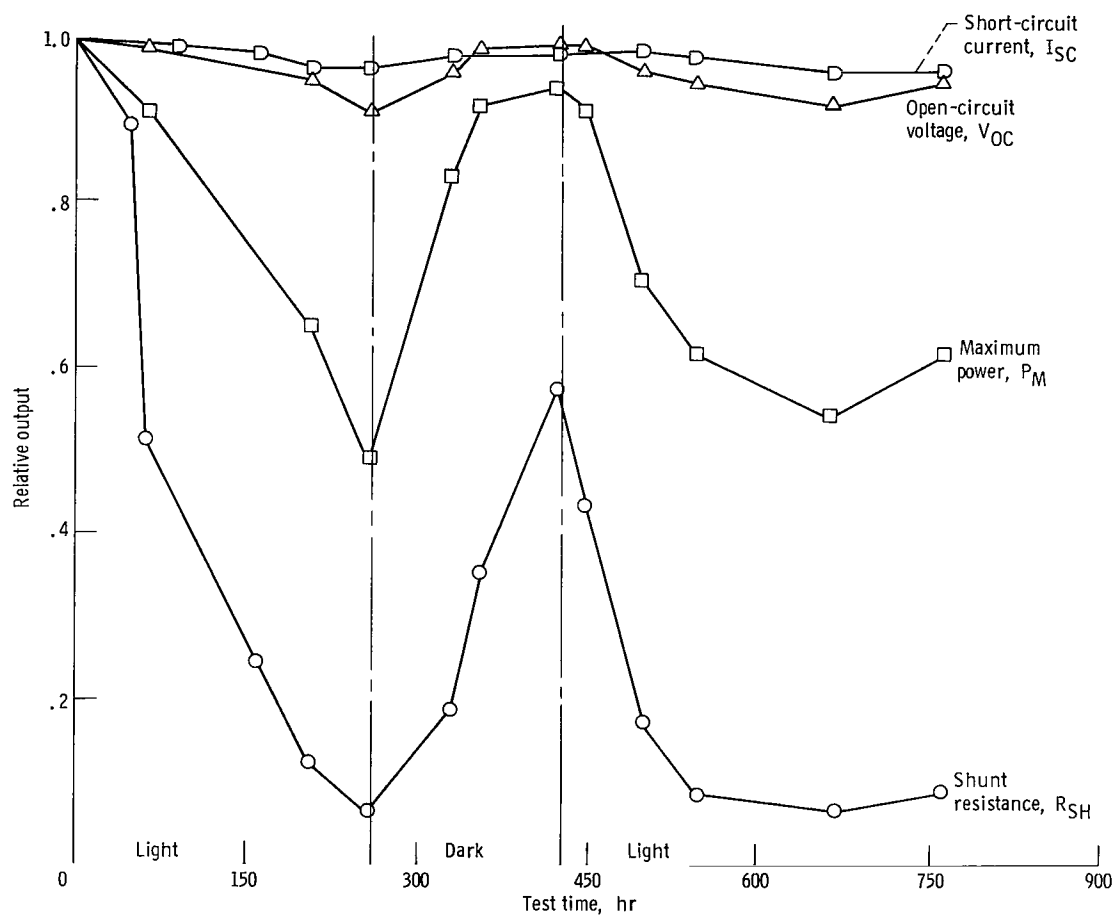


Figure 8. - Relative output as function of time for $\text{Cu}_2\text{S-CdS}$ solar cell exposed to constant illumination and dark storage while at open circuit.

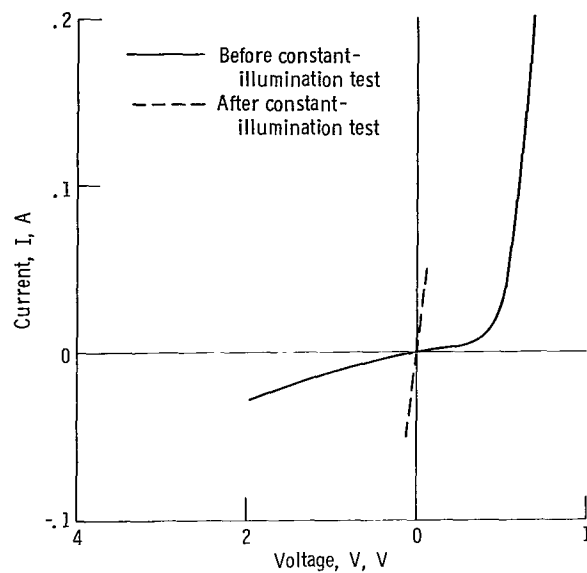


Figure 9. - Dark current-voltage characteristics for Cu_2S -CdS solar cell before and after constant-illumination, open-circuit load test.



Figure 10. - Nodule formed on Lewis cell during constant-illumination, open-circuit voltage test. X210.

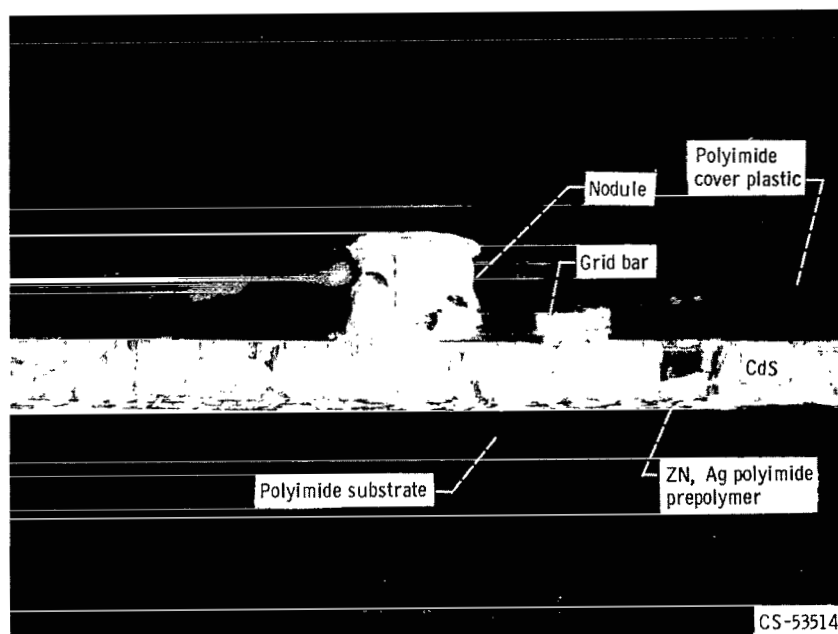


Figure 11. - Cross section of CdS cell showing nodule. X250.

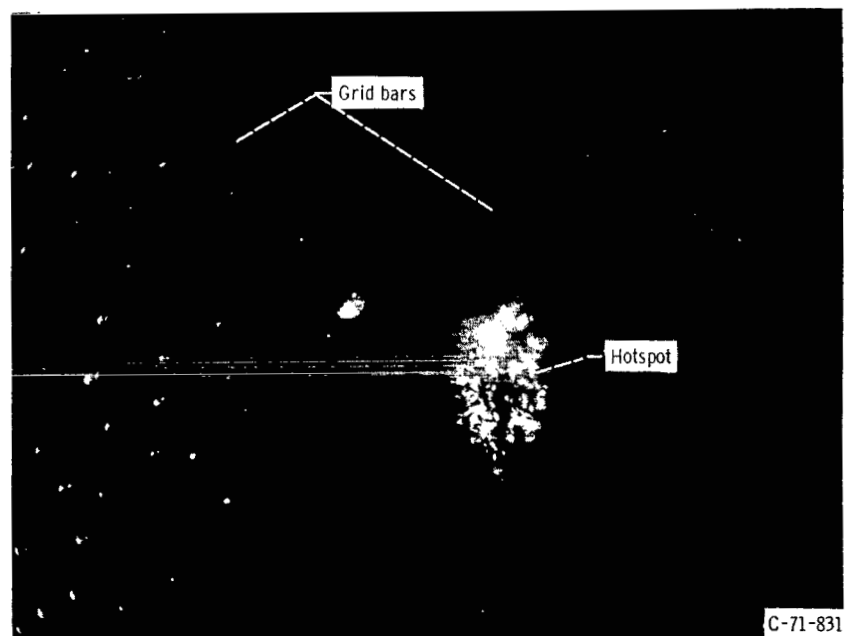


Figure 12. - Hotspot appearing on cell coated with liquid crystals. X200.

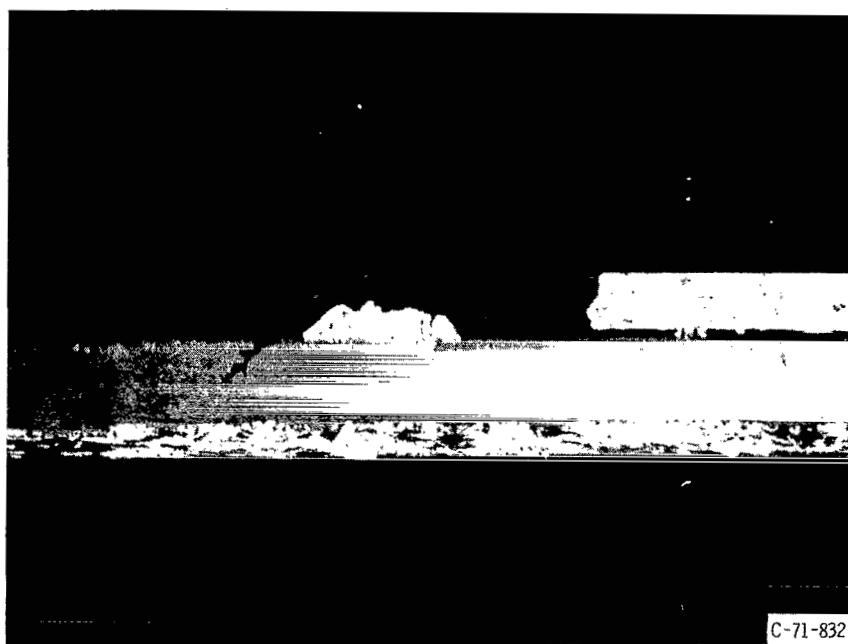


Figure 13. - Copper nodule grown on Cu_2S -CdS solar cell under open-circuit illumination.

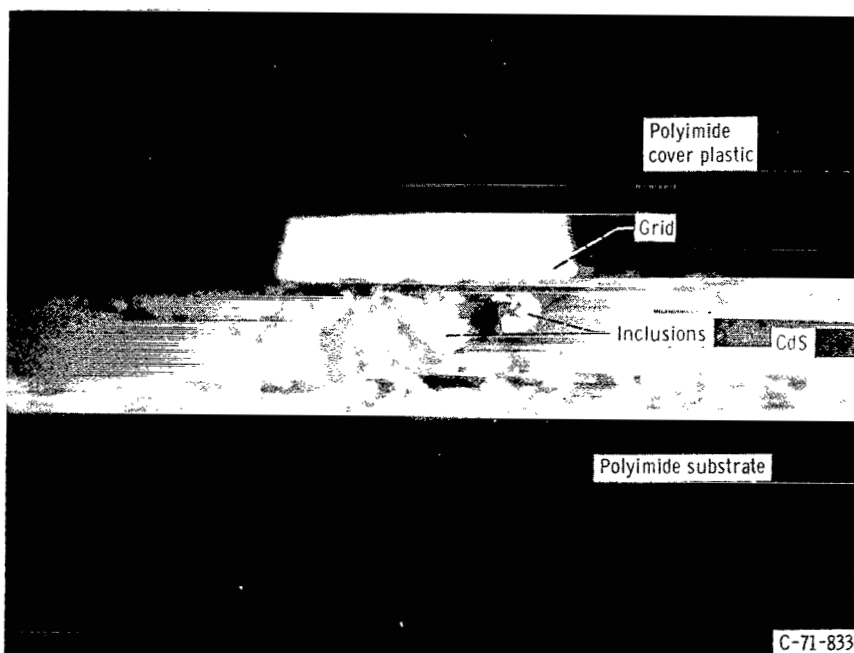


Figure 14. - Inclusions found in hotspot region formed during constant-illumination testing. X500.

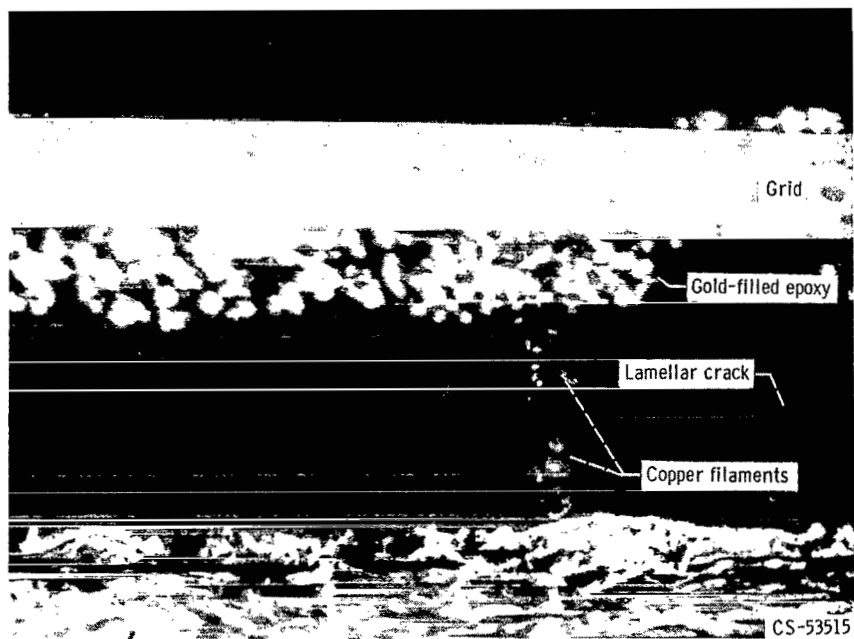


Figure 15. - Cross section of copper filaments in Cu_2S -CdS solar cell. X1000.

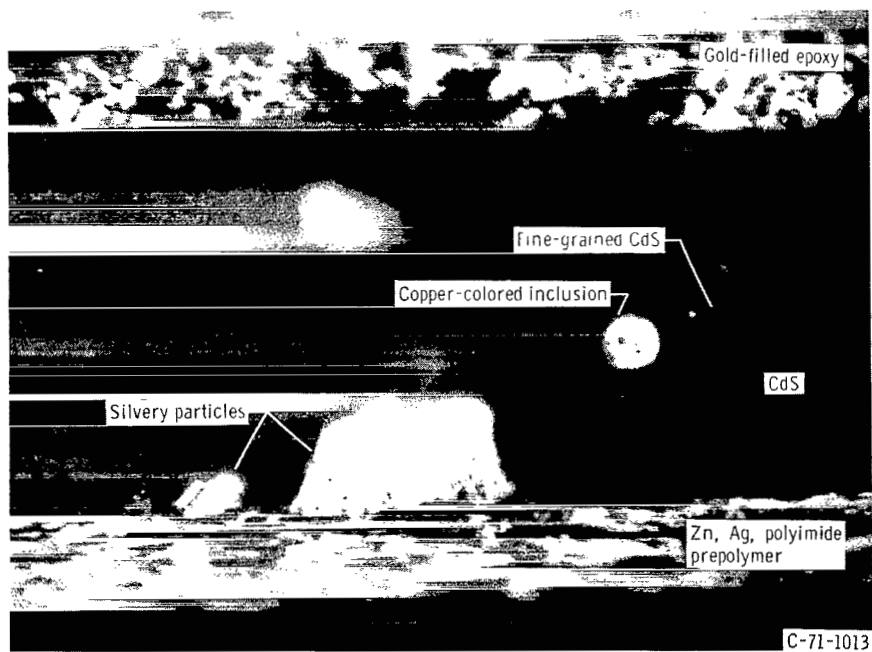


Figure 16. - Cross section of hotspot region inactivated by reverse bias. X1000.

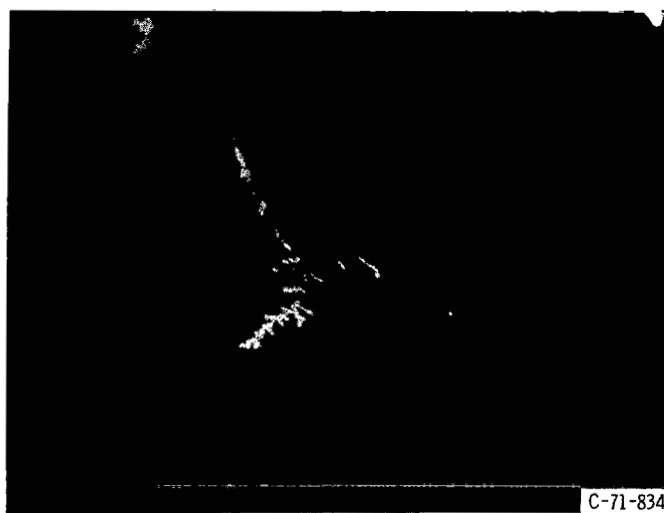


Figure 17. - Dendrite on Cu_2S surface grown with 2.5-V reverse bias. X40.

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